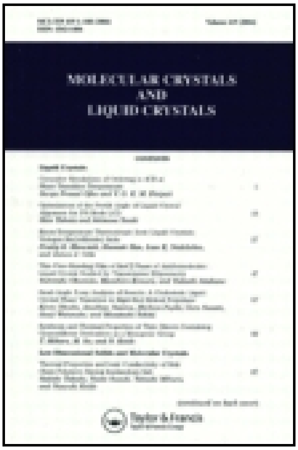

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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O. Phaovibul [a] [b] , S. Denprayoonwong [a] [b] & I. M. Tang [b] [c]

[a] Faculty of Science, Mahidol University, Bangkok, 4, Thailand

[b] Department of Chemistry

[c] Department of Physics

Version of record first published: 20 Apr 2011.

To cite this article: O. Phaovibul , S. Denprayoonwong & I. M. Tang (1981): Fractional Volume Changes of Binary Nematic Mesophase Mixtures at the Nematic Isotropic Transition, Molecular Crystals and Liquid Crystals, 73:1-2, 71-79

To link to this article: http://dx.doi.org/10.1080/00268948108076262

Mol. Cryst. Liq. Cryst., 1981, Vol. 73, pp. 71–79
0026-8941/81/7302-0071 $06.50/0

Printed in the United States of America

Fractional Volume Changes of Binary Nematic Mesophase Mixtures at the Nematic Isotropic Transition

O. PHAOVIBUL†, S. DENPRAYOONWONG† and I. M. TANG‡
Faculty of Science, Mahidol University, Bangkok 4, Thailand

(*Received May 9, 1981*)

The fractional volume changes at the nematic isotropic transitions in binary mixtures of *p*-azoxyanisole (PAA) and 4,4′-di-*n*-hexyloxyazoxybenzene (PHAB) are reported. It is observed that the fractional volume change-composition curve exhibits a depression similar to that seen in the phase boundary of this system. The behavior of the fractional volume change is explained in terms of the binary mesophase mixture theory of Humphries, James and Luckhurst which was able to explain the shape of the phase boundary of the PAA/PHAB system.

I INTRODUCTION

The phase boundaries between the nematic and isotropic phases of several binary nematic mesophase systems have been reported.[1–5] Early attempts[6] to explain the shapes of the nematic-isotropic phase boundaries have used the Chatelier-Schröder-Van Laar (CSL)[7] equations which were originally used to explain the phase boundaries of ideal mixtures. Ivashchenko *et al.*,[8] showed that the CSL equations could not explain the phase behaviors of the phase boundaries of mesophase mixtures which were highly non ideal. Smith[9] and Demus *et al.*,[10] have looked at the conditions under which the CSL equations are valid. They were able to point out the modifications required to make the CSL equations applicable to non ideal mixtures. Demus *et al.*,[10] used the modified CSL equations to explain the phase behaviors of various mixtures of liquid crystals belonging to the homologous series of the 4,4′-di-*n*-alkoazoxy-

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† Department of Chemistry
‡ Department of Physics

benzenes. Recently, Van Hecke[11] showed that the phase boundaries of these mixtures could also be explained on the basis of regular solution theory.

Humphries, James and Luckhurst (HJL)[12] have developed a model which appears to be able to interpret the phase diagrams at the molecular level. Humphries and Luckhurst[13] have applied their theory to explain the behavior of the phase boundaries of several mixtures of the 4,4′-di-*n*-alkoxyazoxybenzenes. Their theory has also been used to explain the shapes of the boundaries of the two-phase region which occurs in mixtures of mesophase and non mesophase solutions.[14]

The purpose of this paper is to study the fractional volume change at the nematic-isotropic transition of binary mixtures of *p*-azoxyanisole (PAA) and 4,4′-di-*n*-hexyloxyazoxybenzene (PHAB). The fraction volume changes at the nematic-isotropic transition of PAA/4,4′-di-*n*-pentyloxyazoxybenzene (PPAB) have been reported by Phaovibul *et al.*[15] An expression for the fractional volume change in a binary nematic mesophase mixture which is described by the HJL model is derived in Section II. In Section III, we present our measurements of the fractional volume changes in PAA/PHAB mixtures at their nematic-isotropic transition. Comparison of the measured values with some predicted fractional volume changes is given.

II THEORETICAL ASPECTS

A Model

In the modified Humphries-James-Luckhurst theory of liquid crystal mixtures, the following two pseudo-potentials were introduced

$$U_1 = -\{[x\epsilon_{11}s_1 + (1-x)\epsilon_{12}s_2]/v\}P_2(\cos\theta_1) \tag{1a}$$

$$U_2 = -\{[x\epsilon_{12}s_1 + (1-x)\epsilon_{22}s_2]/v\}P_2(\cos\theta_2) \tag{1b}$$

where $U_{1(2)}$ is the pseudo potential acting on a component 1(2) molecule; x, the mole fraction of component 1 in the mixture; v, the molar volume of the mixture; ϵ_{ij}, the strength of the interaction between species i and j types of molecules and $s_{1(2)}$ is the order parameter associated with component 1(2) in its pure state. By including the minus signs on the RHS of equations (1a) and (1b), the interaction parameters ϵ_{ij} are made to be positive. Using the above pseudopotentials, the molar Helmholtz free energy for the binary nematic liquid crystal mixtures becomes

$$F_m = -\tfrac{1}{2}N[x^2\epsilon_{11}s_1^2 + 2x(1-x)\epsilon_{12}s_1s_2 + (1-x)^2\epsilon_{22}s_2^2]/v$$
$$-RT[x \ln Z_1 + (1-x) \ln Z_2] \quad (2)$$

where $Z_{1(2)}$ is the partition function for component 1(2) in the mixture. By solving a set of equations which define the order parameters s_1 and s_2, Humphries and Luckhurst[13] were able to determine the temperatures at which the Helmholtz free energy vanish. They were able to obtain fits of the phase boundaries of various mixtures of the 4,4′-di-*n*-alkoxyazoxybenzenes only if the value of the mixed interaction parameter deviated from the value expected from the geometric mean approximation $[\epsilon_{12}^{\text{g.m.a.}} = (\epsilon_{11}\epsilon_{22})^{1/2}]$.

Humphries and Luckhurst were also able to determine the boundaries of the two phase regions occuring in mixtures of mesophase and non mesophase liquids. They predicted that the limiting slope of the nematic phase boundary is given by

$$\beta_n^{\infty} = [1 - (\gamma_n^{\infty}/\gamma_i^{\infty})]/0.418$$

while the limiting slope of the isotropic phase is given by

$$\beta_i^{\infty} = [(\gamma_n^{\infty}/\gamma_i^{\infty}) - 1]/0.418$$

where the ratio $\gamma_n^{\infty}/\gamma_i^{\infty}$ is given by

$$\ln (\gamma_n^{\infty}/\gamma_i^{\infty}) = 0.418[(v_2/v_1) - (\epsilon_{12}/\epsilon_{11})^2]$$

with v_1 and v_2 being the molar volumes of the two constituents. Their results have recently been verified by Jadzyn and Labno's[14] study of mixtures of *p,p′*-*n*-heptyl-cyanobiphenyl and carbon tetrachloride.

B **Fractional Volume Changes**

Since the transition from the nematic to isotropic phase is a first order phase transition, the thermodynamic function of interest is the Gibbs free energy. Using the fact that the Gibbs free energy must be continuous across a first order transition, Chandrasekhar and Madhusudana[16] showed that the fractional volume change at the nematic-isotropic transition is given by

$$\Delta V = -2F_m(\delta F_m/\delta V)_{T=T_{IN}}^{-1}. \quad (3)$$

Using the Helmholtz free energy given by equation (2), we find the fractional volume change at the nematic-isotropic transition in a binary nematic mesophase mixture is given by

$$\begin{aligned}\Delta V/V_n = {} & [2k_BT(x \ln {}_1F_1\{\tfrac{1}{2},3/2,3[x\epsilon_{11}s_1/v + (1-x)\epsilon_{12}s_2/v]/2k_BT\} \\ & + (1-x) \ln {}_1F_1\{\tfrac{1}{2},3/2,3[x\epsilon_{12}s_1/v + (1-x)\epsilon_{22}s_2/v]/2k_BT\})] \\ & - (s_1+1)[x^2\epsilon_{11}s_1/v + x(1-x)\epsilon_{12}s_2/v] - \{(s_2+1)[x(1-x)\epsilon_{12}s_1/v \\ & + (1-x)^2\epsilon_{22}s_2/v]\} X\{\tfrac{1}{2}[x^2\epsilon_{11}s_1^2/v + 2x(1-x)\epsilon_{12}s_1s_2/v \\ & \qquad + (1-x)^2\epsilon_{22}s_2^2]\}^{-1} \qquad (4)\end{aligned}$$

where use is made of the relationship

$$\int_0^1 \exp[A(3\cos^2\theta - 1)/2]\, d(\cos\theta) = \exp(-\tfrac{1}{2}A)\ {}_1F_1(\tfrac{1}{2},3/2,3A/2) \qquad (5)$$

with ${}_1F_1(a,b,c)$ being the confluent hypergeometric function.

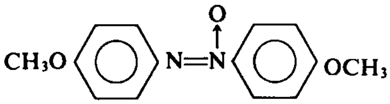
The above expression, Eq. (4), reduces to that of Maier and Saupe[17] in the limits x goes to 0 or 1. As was pointed out by Maier and Saupe, the observed fractional volume changes of the pure nematogens may be used to determine both the values of the order parameter s and the values of the interaction parameter $\epsilon/k_BT_{IN}V$. When the parameters are determined by this means, they no longer have the universal values of 0.4292 and 4.541, respectively. This means that the values of the order parameters and interaction parameters are different for different nematogens.

III EXPERIMENTAL ASPECTS

A Materials

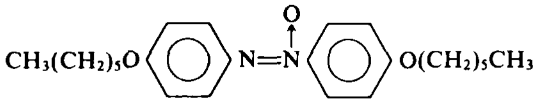
The structural formulas and transition temperatures of the nematogens used in this study are

p-azoxyanisole (PAA)



118°C nematic ⟶ 136°C isotropic

4,4'-di-*n*-hexyloxyazoxybenzene (PHAB)



82°C nematic ⟶ 130.5°C isotropic

The nematogen PAA was obtained from Riedel Co. (Hannover, Germany) while the nematogen PHAB was obtained from Frinton Labs. (Frinton, New Jersey). The samples were recrystallized at least twice from water-ethanol solution before their use in the experiment.

B Experimental Procedures

The densities of the PAA/PHAB mixtures were measured using a standard capillary dilatometer. The details of the experimental procedure are given in Ref. 18. The accuracy of the density measurements is estimated to be ±0.0005 gm/cc.

C Experimental Results

A careful examination of the density data given in Ref. 18 for the PAA/PHAB mixtures and some additional data[19] shows that the molar volumes in the nematic phases of these two mixtures appear to be additive. We have listed in Table I, the molar volumes of several mixtures of PAA/PHAB at 120°C, which is well away from the pretransitional region occuring just below the nematic-isotropic transition. Along with the measured molar volumes, we have listed the ideal mixture molar volumes. As we see, the measured molar volumes agree with the ideal mixture's molar volumes to within the experimental errors of our measurements. Our results does not imply, however, that the molar volumes of the PAA/PHAB mixtures at the nematic side of the transitions are additive. We should not expect the molar volumes to be additive at the transition since the transition is not occuring at a constant temperature and the pretransitional effects are different for different mixtures.

The measured fractional volume changes of the PAA/PHAB mixtures at the nematic-isotropic transition temperatures were obtained by extrapolating the linear portions of the density curves in both the nematic and isotropic phases to the transition temperatures and then measuring the differences at the transition temperature. The differences could be measured to an accuracy corresponding to an error bar of ±0.01% in our fraction volume change values. The results of our measurements are shown in Figure 1.

TABLE I

Molar volumes of binary mixtures of *p*-azoxyanisole (PAA) and 4,4'-di-*n*-hexyloxyazoxybenzene (PHAB) at 120°C.

Mole fraction of PAA in the mixture	Measured Molar Volume (ml/mole)	Ideal Mixture Molar Volume (ml/mole)
PAA	220.342	220.342
0.95	230.499	229.365
0.90	239.506	238.387
0.85	248.206	247.410
0.80	257.247	256.433
0.75	266.828	265.455
0.70	275.836	274.478
0.65	283.257	283.500
0.60	293.526	292.523
0.55	301.613	301.546
0.50	311.575	310.568
0.45	320.526	319.591
0.40	328.469	328.614
0.35	337.153	337.636
0.30	347.185	346.659
0.25	355.324	355.681
0.20	366.192	364.704
0.15	374.101	373.727
0.10	384.303	382.750
0.05	393.134	391.772
PHAB	400.794	400.794

IV DISCUSSION

In the limits $x = 0$ or 1, Eq. (4) reduces to the fractional volume change expression obtained by Maier and Saupe[17] except for the differences in the volume dependences of the interactions. For the pure nematogen expression to yield a fractional volume change of 0.44% for PAA, the interaction parameter and order parameter for PAA must be

$$\epsilon_{11}/k_B T_{IN} V_{PAA} = 4.5518$$

and

$$s_{PAA} = 0.4383$$

where T_{IN} is the measured transition temperature, 409.5°K, and V_{PAA} is the measured molar volume, 223.396 ml./mole, of *p*-azoxyanisole. For the frac-

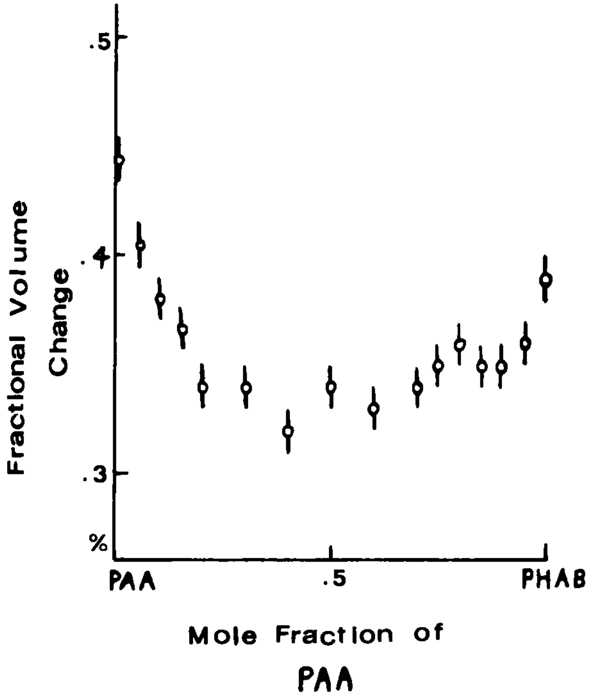


FIGURE 1 Fractional Volume Changes at the Nematic-Isotropic Transitions of Binary Mixtures of *p*-Azoxyanisole and 4,4'-di-*n*-hexyloxyazoxybenzene. The fractional volume changes were obtained by extrapolating the linear portion of the density curves in both the nematic and isotropic phases to the nematic-isotropic temperatures and then measuring the differences at the transition.

tional volume change of PHAB to be 0.39%, the interaction parameter and order parameter of PHAB must be

$$\epsilon_{22}/k_B T_{IN} V_{PHAB} = 4.5507$$

and

$$s_{PHAB} = 0.4376$$

where T_{IN} is the measured transition temperature, 403°K, and V_{PHAB} is the measured molar volume, 404.537 ml./mole, of *p,p'*-di-*n*-hexyloxazoxybenzene (PHAB). To obtain the above values, a sixteen point Gaussian quadrature integration formula was used to numerically evaluate the confluent hypergeometric function ${}_1F_1(a,b,c)$.

The above values for the transition temperatures and molar volumes yield the following interaction parameters

$$\epsilon_{11} = 4.16402 \times 10^5 k_B \text{ deg. ml./mole}$$

and

$$\epsilon_{22} = 7.42814 \times 10^5 k_B \text{ deg. ml./mole}$$

for use in Eq. (4). In the geometric mean approximation, the mixed interaction parameter ϵ_{12} would have the value $5.56156 \times 10^5 k_B$ deg. ml./mole. This value, however, produces negative fractional volume changes for the PAA/PHAB mixtures if it is used in Eq. (4). Adjusting the mixed interaction parameter to $5.34676 \times 10^5 k_B$ deg. ml./mole, using the measured molar volumes and the transition temperatures as determined by the best fit curve, Figure 1 of Ref. 18, the predicted fractional volume changes for the 0.8 mole fraction PAA/0.2 mole fraction PHAB mixture, the 0.5 mole fraction PAA/0.5 mole fraction PHAB mixture and the 0.3 mole fraction PAA/0.7 mole fraction PHAB mixture are 0.38 ± 0.10%, 0.29 ± 0.10% and 0.39 ± 0.10%, respectively. The large error bars in the predicted values are due to the uncertainties in the molar volume measurements (these uncertainties being due to the fact that the densities could only be measured to an accuracy of 0.0005 gm./ml.). The fractional volume change expression, Eq. (4), is extremely sensitive to small errors in various parameters. An error of 0.1°K in the temperature measurements results in the fractional volume changes for the 0.5 mole fraction mixture being 0.24% instead of the 0.29% while an error in the third decimal place of the mixed interaction parameter produces a change from 0.29% to 0.31%. The extreme sensitivity of the equation should not be surprising since the numerator of Eq. (4) is the difference between two quantities which differ only in the third decimal place. The fractional volume change expression, Eq. (4), is, however, able to predict the depression occuring in the fractional volume change curve shown in Figure 1.

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